
Theoretical Investigations on 1,2-Ethanediol: The Problem of Intramolecular Hydrogen Bonds

STEPHAN REILING and JÜRGEN BRICKMANN*

Institut für Physikalische Chemie I, Technische Hochschule Darmstadt, Petersenstrasse 20, D-64287 Darmstadt, Germany

MICHAEL SCHLENKRICH

Chemistry and Health Industry Marketing, Silicon Graphics Basel, Erlensträsschen 65, 4125 Riehen, Switzerland

PHILIPPE A. BOPP

Laboratoire de Spectroscopie Moléculaire et Cristalline, Université de Bordeaux I, 351 Cours de la Liberation, F-33405 Talence Cedex, France

Received 9 March 1994; accepted 23 December 1994

ABSTRACT

The conformational space of 1,2-ethanediol is studied on the basis of *ab initio* and semiempirical calculations. All possible conformers are treated. The relative energies of the conformers are systematically studied using various basis sets up to 6-311 + G(3df, 3pd) in order to perform calculations as accurate as possible within a reasonable amount of computer time. Electron correlation is included using Møller-Plesset perturbation theory. We propose two methods to evaluate the basis set superposition error associated with the intramolecular hydrogen bond appearing in some of the conformers. The results of semiempirical calculations are compared with these *ab initio* calculations. © 1996 by John Wiley & Sons, Inc.

*Author to whom all correspondence should be addressed.

Introduction

Over the last few decades, quantum mechanical calculations have evolved from a method with only a narrow applicability, used only by specialists with theoretical interests, into a valuable tool used to obtain insight into all kinds of molecular properties for which experimental data are not amenable. The reasons for this are (1) the dramatic increase in the speed of computer hardware and software algorithms, which allows us to treat small to medium-sized systems with sufficient accuracy; and (2) the development of modern *ab initio* programs, which are easy to use even by nonspecialists. The data obtained by *ab initio* calculations are often used as input for other theoretical methods. In the field of parameterization of molecular mechanics force fields, the results of *ab initio* calculations are, in addition to experimental data, the most important source for the determination of parameters.

Whereas for experimental methods the error margins for a certain class of molecules are almost always considered, this is rarely done in theoretical studies. For the evaluation of intermolecular nonbonded interactions by supermolecule calculations, however, the applicability of quantum mechanical methods and the resulting errors were extensively investigated.^{1,2} These errors are due to two principal sources: (1) the restricted number of basis functions, which reduces the flexibility for the description of the electron distribution; and (2) the necessarily limited inclusion of electron correlation (e.g., by the commonly used Møller-Plesset second-order perturbation theory, MP2). Both components have different effects on the hypersurface of a molecule and cannot be quantified easily.

The contributions to the total energy associated with molecular deformations originating from bond stretching, valence angle deformation, and torsional rotations are already reproduced by moderate basis sets [e.g., 6-31G* (see ref. 3) and MP2], but only for molecules in the ground state containing single bonds only in a "relaxed" conformation. This is not true if nonbonded intramolecular interactions become important, especially H bonds (e.g., in polyalcohols).

The determination of nonbonded interactions is always accompanied by the problem of the basis set superposition error (BSSE). This error can be estimated for interactions between separate

molecules using, for example, the counterpoise (cp) method suggested by Boys and Bernardi.⁴ In the case of water dimers,¹ the BSSE was found to be on the order of 1 kcal/mol. In many studies it was shown that BSSE-corrected energy hypersurfaces give "better" physical results for hydrogen-bonded systems than uncorrected ones. Little attention was paid to these considerations for intramolecular interactions. In the present study we determine the level of theoretical (computational) effort that is necessary to obtain reliable results, especially with respect to the relative energy of conformers, using the example of glycol (1,2-ethanediol).

In the first section of this study, the influence of growing basis set size and inclusion of electron-electron correlation are investigated, leading to geometries for all possible conformers of 1,2-ethanediol. In the second section, the relative energies of these conformers are compared using different basis sets up to MP2/6-311++G(3df,3pd). The influence of higher terms of Møller-Plesset perturbation theory is also investigated in this section. As a result of the latter section, the minimum level of theoretical effort required to obtain relative energies of the various conformers is determined. Since one is interested in performing *ab initio* calculations with a minimum amount of computer resources, we will investigate in the third section the possibilities of correcting the results of smaller basis sets. This is done by estimating the intramolecular BSSE connected to the presence or absence of H bonds. Two methods to estimate the intramolecular BSSE are presented. In the fourth and last section, the applicability of semiempirical methods for this class of molecules is tested by using various semiempirical Hamiltonians. The newly derived complete set of geometries of 1,2-ethanediol conformers is included as Appendix A.

Outline of the Procedure

1,2-Diols have been studied both experimentally⁵ and theoretically⁶⁻¹³ in context with the analysis of intramolecular hydrogen bonds. 1,2-Ethanediol is a molecule which is small enough to calculate properties of H-bonded systems with a moderate amount of computer time. After the first work of van Alsenoy,¹¹ who performed geometry optimizations on a 4-21G level, new results obtained by HF/6-31G*, HF/6-31G**, and MP2/6-31G* calculations have been published in recent

years.^{6,9} Since not all of the conformations of the molecules were studied in these publications, we extend them here, lowering on that occasion the margin of error for the energies.

The formation of an intramolecular H bond in 1,2-ethanediol can be compared with the formation of a five-membered ring, in which an optimum arrangement of atoms with respect to the H bond cannot be obtained. The backbone of the molecule comprises three torsions (the central O—C—C—O torsion and both the H—O—C—C torsions). Assuming three minima per torsion ($g = 60$, $t = 180$, $g' = -60$), this leads to $3^3 = 27$ possible stable conformations. Considering the symmetry of the conformations, this number is reduced to 10 unique conformations. The naming convention for the conformers in this article is taken from Radom et al.¹⁰: Each conformer is identified by the angles of its three backbone torsions, the central one being denoted by a capital letter (e.g., tGg'). G conformations (or T conformations) mean all conformations with a gauche (or trans) position in their central torsion. Schematic geometries of the 10 conformers of 1,2-ethanediol are shown in Figure 1. They are discussed in the following paragraph.

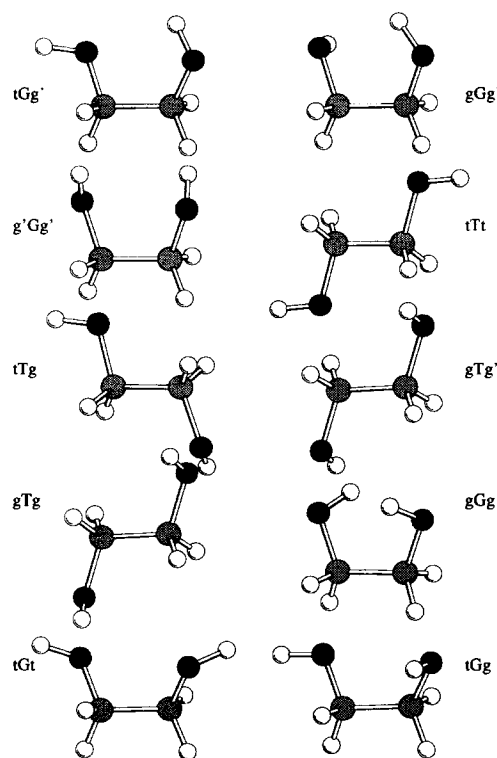


FIGURE 1. Geometries of the ten 1,2-ethanediol conformers.

The 10 conformers can be subdivided in three groups: H-bonded G conformations and non-H-bonded G and T conformations. The conformers tGg' and gGg' both have a single H bond. Due to the increased repulsion, gGg' is energetically higher than tGg' . The conformation $g'Gg'$ shows two weak H bonds, but the energy gain in forming these two weak H bonds is in opposition to the strain of the whole structure. This is therefore the highest in energy of all H-bonded conformers. The four conformers tTt , tTg , gTg' , and gTg , differ only in the positions of the two O—H groups. None of these conformers contain an H bond; therefore, their energy difference will mainly be due to the torsional energy of the O—H groups and possibly also to a dipole-dipole interaction between both O—H groups. The three conformations gGg , tGt , and tGg are the highest in energy. They show no H bond but an increased non-bonded dipole-dipole repulsion between the two O—H groups, compared to the T conformations.

Ab Initio Calculations

GEOMETRY OPTIMIZATION OF THE CONFORMERS

We took the results of van Alsenoy¹¹ as a starting point to derive improved geometries on a 6-31G** and MP2/6-31G** level. All *ab initio* calculations were performed using GAUSSIAN 90¹⁴ on a Cray YMP 8/832 and a Siemens VP S600/20. The torsional angles and the O—H distances are shown in Tables I (HF/6-31G**) and II (MP2/6-31G**). These data are sufficient for a discussion of the geometries (the complete set of geometric data is listed in Appendix A). As the determination of MP2 geometries requires a great amount of

TABLE I.
HF/6-31G** Geometries of the Glycol Conformers
(Torsional Angles in Degrees, Distances in Å).

	$\tau_{H1-O1-C1-C2}$	$\tau_{O1-C1-C2-O2}$	$\tau_{H2-O2-C2-C1}$	r_{O2-H1}	r_{O1-H2}
tGg'	-169.95	60.66	-53.82	2.36	3.58
gGg'	76.04	57.81	-45.50	2.36	3.27
$g'Gg'$	-81.79	57.34	-81.10	2.68	2.69
tTt	180.00	180.00	180.00	4.26	4.26
tTg	-175.89	180.01	75.47	3.92	4.32
gTg'	73.79	-179.96	73.79	3.95	3.95
gTg	70.77	177.69	70.78	3.95	3.95
gGg	45.45	50.00	45.97	2.90	2.89
tGt	-165.04	72.41	-165.02	3.61	3.61
tGg	-177.91	63.87	59.18	3.19	3.73

TABLE II. **MP2/6-31G** Geometries of the Glycol Conformers (Torsional Angles in Degrees, Distances in Å).**

	τ_{H1O1C1C2}	τ_{O1C1C2O2}	τ_{H2O2C2C1}	τ_{O2H1}	τ_{O1H2}
tGg'	-165.79	60.04	-50.39	2.24	3.53
gGg'	72.86	55.43	-42.19	2.23	3.19
g'Gg'	-77.68	55.50	-77.82	2.58	2.58
tTt	180.00	180.00	180.00	4.27	4.27
tTg	-175.84	179.61	71.95	3.91	4.34
gTg'	70.43	-179.98	-70.43	3.95	3.95

computer time, we only used this formalism for the six conformers which are lowest in energy. Our geometric results are compared to the 4-21G results of van Alsenoy¹¹ in the following discussion.

The geometric variables shown in Tables I and II can, in principle, be divided into two sets: geometric variables defined by atoms involved in H bonds and geometric variables defined by atoms not involved in H bonds. The first set consists of the H bonds and g' and G torsions of the conformers tGg', g'Gg', and gGg'. The second set contains all other variables. The numerical values of the first set of geometric variables increase from HF/4-21G to HF/6-31G** derived geometries due to an increased H-bond distance. The numerical values of variables of the second set decrease. Both sets of variables show the same trend when electron correlation is included. The numerical values decrease, and the molecular structure contracts. The changes from HF/4-21G to HF/6-31G** are in the range of 9° and 0.4 Å, and the changes from HF/6-31G** to MP2/6-31G** are in the range of 3° and 0.1 Å.

There are only small differences between MP2/6-31G** and HF/6-31G** derived geometries. Since the MP2/6-31G** calculations require much more computer time, all further studies are based on the HF/6-31G** geometries. The geometries of all conformers of glycol are determined on this basis. It will be shown that the relative energies between conformers are rarely influenced by the small variations in geometries, whereas they are strongly dependent on the basis set. In previous studies¹⁵ it was shown that changes in geometry due to different basis sets and the inclusion of electron correlation are small. In comparison to the HF/6-31G*-derived geometries of Nagy et al.,⁵ the geometries derived here show elongated O—H bonds, by about 0.01 Å. The angles are nearly unaffected by the additional polarization functions (deviations smaller 1°), but the torsional angles differ by up to 4°.

RELATIVE ENERGIES

The energies of the conformers were calculated using Pople's basis sets 6-31G**, 6-311 + G(2d, 2p), and 6-311 + + G(3df, 3pd).³ Furthermore, the D95** basis set and the TZP and TZ2P basis sets were used.³ All basis sets are listed in Table III along with the number of their basis functions and the contraction schemes. These are the most commonly used basis sets for *ab initio* calculations of H-bonded systems. The basis sets D95** (94 basis functions) and 6-31G** (90 basis functions) are of comparable size and differ mostly in the contraction scheme. The same situation is found in comparing the basis sets 6-311 + G(2d, 2p) (162 basis functions) and TZ2P (154 basis functions). These two pairs of basis sets will be compared in detail in the subsequent discussion. In the following the energies of the glycol conformers are given relative to the absolute energies and the conformer tGg', which is the lowest in energy:

$$\Delta E_{\text{conf}} = E_{\text{conf}} - E_{\text{tGg'}} \quad (1)$$

We calculated energies on the basis of MP2/6-31G** and HF/6-31G** geometries with different basis sets in order to test the dependence of the results on the geometries. The results of these Hartree-Fock (HF) and MP2 calculations are given in Tables IV and V.

Only small differences of 0.2 kcal/mol or less are found between the relative energies calculated with the different geometries (see Tables IV and V). The ranking order in the relative energies is not affected by the geometries. This is in agreement with the results of Friesner,¹⁶ who states that geometries converge faster to the "final" result in *ab initio* calculations than energies. The relative energies of the HF/6-31G** derived conformers strongly depend on the basis set but converge with increasing number of basis functions. The

TABLE III. **Basis Sets Employed and the Number of Their Uncontracted / Contracted Basis Functions.**

No.	basis set	uncontracted	contracted	number of uncontracted/contracted basis functions
0	4-21G	7s3p/2s	3s2p/2s	84/48
1	6-31G(d,p)	10s4p1d/4s1p	3s2p1d/2s1p	154/90
2	D95(d,p)	9s5p1d/4s1p	4s2p1d/2s1p	162/94
3	TZP	10s6p1d/5s1p	6s3p1d/3s1p	180/116
4	TZ2P	10s6p2d/5s2p	6s3p2d/3s2p	218/154
5	6-311+G(2d,2d)	12s6p2d/5s2p	5s4p2d/3s2p	226/162
6	6-311++G(3df,3pd)	12s6p3d1f/6s3p1d	5s4p3d1f/4s3p1d	328/264

TABLE IVa.
Relative Energies (kcal / mol) of the Glycol
Conformers, Calculated with Various Basis Sets on
HF / 6-31G Geometries.**

	6-31G**		6-311+G(2D,2P)		6-311++G(3DF,3PD)	
	HF	MP2	HF	MP2	HF	MP2
tGg'	0.00	0.00	0.00	0.00	0.00	0.00
gGg'	0.64	0.19	0.69	0.50	0.68	0.42
g'Gg'	1.28	1.22	1.03	1.06	1.05	0.94
tTt	2.03	3.22	1.69	2.63	1.65	2.60
tTg	2.35	3.24	2.08	2.83	2.01	2.77
gTg'	2.43	2.96	2.28	2.86	2.22	2.79
gTg	2.80	3.27	2.59	3.09	2.49	2.99
gGg	3.36	3.43	3.04	3.29	2.96	3.21
tGt	3.65	4.21	2.90	3.24	2.77	3.14
tGg	4.10	4.39	3.46	3.78	3.29	3.59

TABLE IVb.
Relative Energies (kcal / mol) of the Glycol
Conformers, Calculated with Various Basis Sets on
HF / 6-31G Geometries.**

	D95**		TZP		TZ2P	
	HF	MP2	HF	MP2	HF	MP2
tGg'	0.00	0.00	0.00	0.00	0.00	0.00
gGg'	0.71	0.24	0.93	0.49	0.62	0.34
g'Gg'	1.34	1.31	1.43	1.37	1.03	0.98
tTt	2.00	3.12	1.81	3.08	1.73	2.72
tTg	2.35	3.10	2.33	3.22	2.05	2.82
gTg'	2.40	2.77	2.59	3.10	2.20	2.76
gTg	2.80	3.12	2.98	3.45	2.50	3.01
gGg	3.12	3.04	3.28	3.23	2.97	3.24
tGt	3.50	4.10	3.27	3.78	2.87	3.30
tGg	3.93	4.22	3.91	4.22	3.36	3.72

Hartree-Fock energies listed in Table IV are plotted as functions of the basis set number (Table III) in Figure 2. It is evident that the differences in relative energy become smaller with increasing number of basis functions. From 4-21G to 6-311 + G(3df, 3pd), the relative energy of the conformation tGg (the conformer highest in energy) is reduced from 6.44 kcal/mol to 3.29 kcal/mol at the Hartree-Fock level. This is a reduction by 50%. There is a systematic decrease in the energy difference to tGg' with increasing number of basis functions. Only two conformers, gGg and tGt, change their energetical order. While the HF/6-31G** energy of tGt is 0.29 kcal/mol higher than that of gGg, it is 0.19 kcal/mol lower in the HF/6-311 + G(3df, 3pd) calculation.

The same general trend of a systematic decrease of the relative energies, as a function of increasing basis set size, is also found in the MP2 calculations (see Fig. 3), but the effect is not as strong as in the HF calculations. The relative energies are given in

Tables IV and V. Table VI shows the energetical orders obtained with the different basis sets. The relative energies are plotted as functions of the basis set number in Figures 3 and 4. For the conformer tGg, the relative energy is reduced from 4.39 kcal/mol (MP2/6-31G**) to 3.59 kcal/mol [MP2/6-311 + G(3df, 3pd)].

The contribution of MP2 to the relative energies of the three conformers containing H bonds is in the range of -0.45 to +0.03 kcal/mol. The contribution to the other conformers is larger and varies from -0.08 to +1.26 kcal/mol. The energetical order of the conformers is strongly influenced by the inclusion of correlation. Only the three lowest energy conformers (tGg', gGg', and g'Gg') and the highest energy conformer (tGg) keep their ranking positions with increasing number of basis functions. Various changes appear in the ranking order with increasing basis set size. It is interesting to note that the ranking order of the Hartree-Fock and MP2 energies is identical on the level of the two largest basis sets 6-311 + G(2d, 2p) and 6-311 + G(3df, 3pd).

The most important change in going from HF- to MP2-derived relative energies is the appearance of an energy gap between conformers with (tGg', gGg', and g'Gg') and without H bonds. This effect can be assigned to the intramolecular nonbonded interactions, which can only be reproduced correctly by the inclusion of electronic correlation.^{1, 2, 6, 15, 17} On the MP2 level, the ranking order is unstable, not only with respect to the size but also with respect to the type of the basis set. By changing from 6-31G** (No. 1, 90 basis functions) to D95** (No. 2, 94 basis functions), the energetical order is remarkably changed. The non-H-bonded conformer gGg is reduced in relative energy and appears to be even lower in energy than three of the four T conformers. With the increasing number of basis functions, this conformer rises systematically in relative energy (from position 6 to 9). Even on the level of TZ2P (No. 4) and 6-311 + G(2d, 2p) (No. 5), the changes in relative energy are sufficient to allow two pairs of conformers to exchange places (gTg', tTg and gGg, tGt). The changes in relative energy appearing at this level are surprisingly high, especially the changes within the three triple-zeta basis sets TZP, TZ2P, and 6-311 + G(2d, 2p). An identical order of the energies is found with 6-311 + G(2d, 2p) and with the much more computer time intensive 6-311 + G(3df, 3pd) basis set.

The systematic decrease of the relative energy of the conformers without H bonding (the HF and

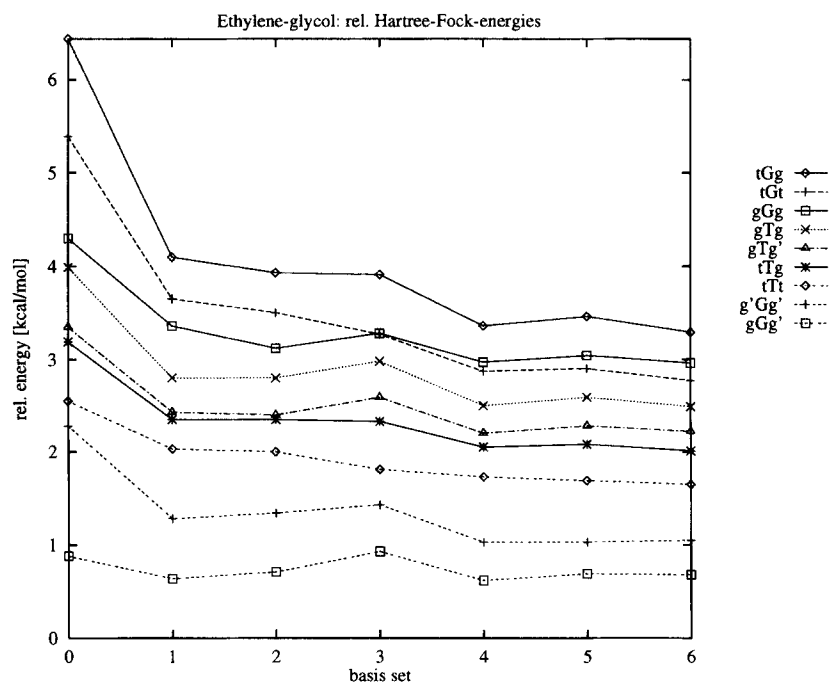


FIGURE 2. Relative Hartree-Fock energies of the glycol conformers as a function of the basis set used. Basis set numbers refer to Table III.

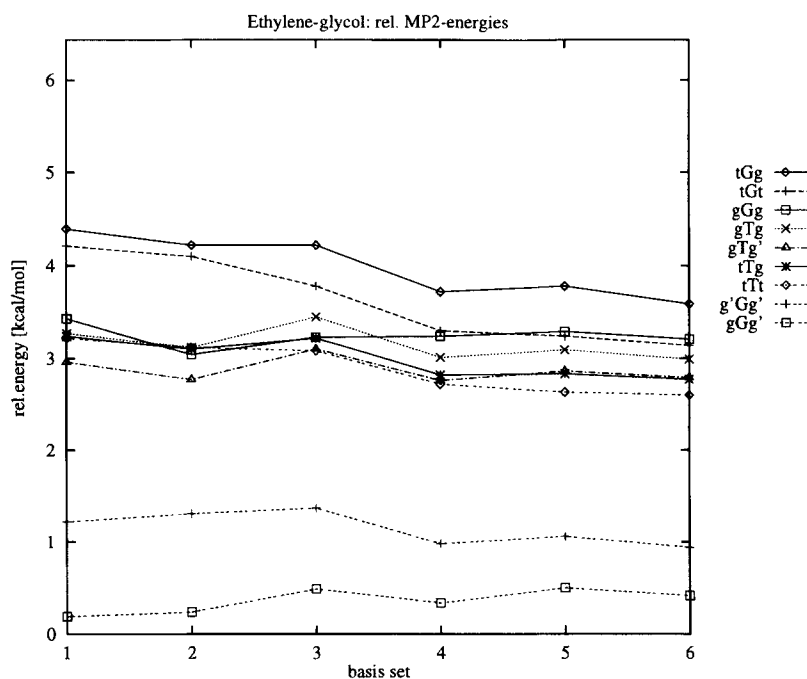


FIGURE 3. Relative MP2 energies of the glycol conformers as a function of the basis set used. Basis set numbers refer to Table III.

TABLE V.
Relative Energies (kcal / mol) of the Glycol Conformers, Calculated with Various Basis Sets on MP2 / 6-31G** Geometries.

	6-31G**		6-311+G(2D,2P)	
	HF	MP2	HF	MP2
tGg'	0.00	0.00	0.00	0.00
gGg'	0.71	0.15	0.81	0.55
g'Gg'	1.28	1.23	1.10	1.19
tTt	1.88	3.33	1.45	2.63
tTg	2.22	3.37	1.83	2.82
gTg'	2.35	3.06	2.09	2.84

TABLE VI.
Energetical Order of the 1,2-Ethanediol Conformers with the Different Basis Sets on the MP2 Level.

6-31G**	D95**	TZP	TZ2P	6-311+G(2d,2p)	6-311++G(3df,3pd)
tGg'	tGg'	tGg'	tGg'	tGg'	tGg'
gGg'	gGg'	gGg'	gGg'	gGg'	gGg'
g'Gg'	g'Gg'	g'Gg'	g'Gg'	g'Gg'	g'Gg'
gTg'	gTg'	tTt	tTt	tTt	tTt
tTt	gGg'	gTg'	gTg'	tTg	tTg
tTg	tTt	tTg	tTg	gTg'	gTg'
gTg	tTt	gGg	gTg	gTg	gTg
gGg	gTg	gTg	gGg	tGt	tGt
tGt	tGt	tGt	tGt	gGg	gGg
tGg	tGg	tGg	tGg	tGg	tGg

MP2 calculations) can be assigned to the BSSE in the reference *tGg'* conformer. This BSSE leads to an overestimation of the H-bond interaction energy, which is gradually reduced with increasing size of the basis set. The importance of the intramolecular H bond for the relative energies is also seen from the drastic changes which occur when electron correlation is included. Attractive nonbonded dispersion interaction occurring between the O—H groups can only be described with post-HF methods. The changes of relative energies within the groups (H-bonded and non-H-bonded conformers) cannot, however, be completely explained by correlation effects. As a test for the contribution of higher perturbation terms, we calculated MP3 and MP4 energies for the conformers *tGg'* and *tTt* on the MP2/6-31G** geometries (see Table VII for the relative energies) and found that the contributions of the higher terms cancel each other out. This is known for other systems containing H bonds—for example, water dimers^{1,2} and glycol.¹²

CORRECTION OF THE INTRAMOLECULAR BSSE

The relative energies of the different conformers are calculated as the differences of the absolute

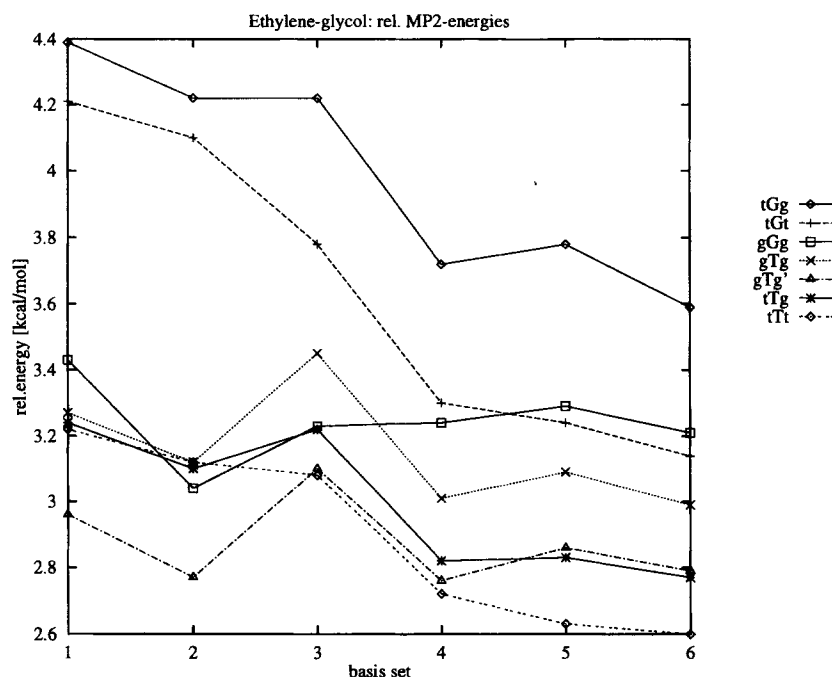


FIGURE 4. Relative MP2 energies of the glycol conformers number tTt to tGg as a function of the basis set used. Basis set numbers refer to Table III.

TABLE VII.
Relative Energy of the Conformer *tTt* (kcal / mol),
Calculated Including MP2, MP3, and MP4
Perturbation Theory.

MP2/6-31G**//MP2-6-31G**	3.33
MP3/6-31G**//MP2/6-31G**	2.94
MP4/6-31G**//MP2/6-31G**	3.29

energies and that of the lowest energy conformer *tGg'*, according to eq. (1). Each conformer is affected with a BSSE, depending on the existence or nonexistence of intramolecular interactions (e.g. H bonds):

$$\Delta E_{\text{conf}} = E'_{\text{conf}} - E_{\text{conf}}^{\text{BSSE}} - E'_{tGg'} + E_{tGg'}^{\text{BSSE}} \quad (2)$$

where E' is the energy of the conformer without BSSE and E^{BSSE} is the BSSE energy of the conformer. Hence the correct relative energy would be

$$\Delta E_{\text{conf}}^{\text{corr}} = \Delta E_{\text{conf}} - \Delta E^{\text{BSSE}} \quad (3)$$

where

$$\Delta E^{\text{BSSE}} = E_{tGg'}^{\text{BSSE}} - E_{\text{conf}}^{\text{BSSE}} \quad (4)$$

The basis of the energy scale used to calculate the relative energies of a conformer is the conformer *tGg'*, which contains an intramolecular H bond. All other conformers contain weaker (*gGg'*, *g'Gg'*) or no H bonds. Therefore, a complete cancellation of the BSSE cannot be expected. From the previous discussion, it is obvious that the BSSE has the largest effect when conformers with a different number of H bonds are compared, since a partial cancellation of the error can be expected only if both conformers contain the same number of H bonds.

A standard method used to determine the BSSE in supermolecule calculations is the counterpoise method (cp method) introduced by Boys and Bernardi.⁴ Modified cp methods (e.g., polarization cp^{18,19}) have been suggested to determine the BSSE more accurately. The discussion whether the cp method overestimates the BSSE or not²⁰⁻²⁶ notwithstanding, the cp method is nevertheless the most widely used method. In this section we propose two methods to correct the errors in the relative energies produced by the BSSE. Both are based on the cp method.

The cp method was developed for intermolecular BSSE and is outlined as follows: To determine the BSSE of a complex of n monomers, the energy of each monomer is calculated alone (E_{monomer}) and with ghost atoms (no electrons, no nuclei; only

basis functions) in the place of the atoms of all other monomers ($E_{\text{monomer}}^{\text{cp}}$). The energy associated with the BSSE is then given by

$$E^{\text{BSSE}} = \sum_1^n E_{\text{monomers}} - \sum_1^n E_{\text{monomers}}^{\text{cp}} \quad (5)$$

It is obvious that this procedure cannot be applied to intramolecular H bonds. The "monomers" forming an H bond are parts of the same molecule, and simply replacing a "monomer" by ghost atoms would not yield reasonable results. The replacement of a part of the molecule by ghost atoms would lead to new nonbonded overlaps in place of the broken bonds and would overestimate the BSSE, not to mention the practical difficulties of performing unrestricted Hartree-Fock (UHF) calculations. In the following, two new methods for the determination of the intramolecular BSSE are discussed for the two conformers *tGg'* and *tTt*. These conformers differ in their number of H bonds. The conformer *tGg'* with one H bond will be energetically favored in comparison with the conformer *tTt* (no H bond): In the region of the H bond, the local flexibility of the basis is increased due to functions centered on the neighboring atoms (nonbonded overlap).

The first method to estimate this BSSE is termed the additive counterpoise method (acp method). The goal of the acp method is to compensate the energetical reduction of the conformer with the greater number of H bonds by adding ghost atoms to the conformer with less H bonds, leading to "virtual" nonbonded overlaps and the same local increase of the number of basis functions as in the other conformer. The method is characterized as follows (see Figure 5):

1. The H-bond distances and the H-bond angles of the conformer containing H bonds are extracted.
2. Ghost atoms are added to the conformer containing no H bonds with the distance and angle obtained in the previous step. The position of the ghost atoms is now determined except that of one rotational degree of freedom around the H—O bond.
3. The final position of the ghost atoms is found by minimizing the virtual nonbonded interactions of these ghost atoms with the rest of the molecule with respect to this rotational degree of freedom.

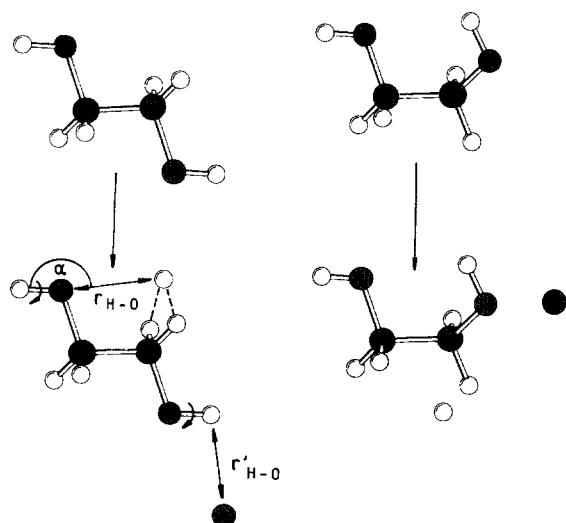


FIGURE 5. For the estimation of the BSSE between two conformers by the acp-method dummy atoms are added to represent the non-bonded overlap of the H-O-groups in the referenced conformer. This is shown for the examples of the conformers *tTt* (left) and *tGg'* (right).

4. To keep the total number of basis functions constant and to compensate for newly generated nonbonded overlaps of the added ghost atoms with atoms of the conformer, the same number of ghost atoms is added to the conformer with more H bonds, using the previously described algorithm.

The method results in two conformers with the same number of ghost atoms added (in the example here, two ghost atoms). The change in the relative energy of these two conformers calculated with and without the ghost atoms is the ΔE^{BSSE} .

The second method is termed the equivalence counterpoise method (ecp method). Here the positions of the O—H groups of a conformer are extracted and hydrogens are added to generate an H_2O dimer with the same arrangement of H bonds as in the glycol conformer. For this H_2O dimer, the BSSE can be calculated in the usual way (see Fig. 6). The BSSE is thus not calculated for the conformer itself, but for an H_2O dimer with equivalent H bonds. ΔE^{BSSE} is calculated according to eq. (4). The BSSE can be determined for every conformer, and the calculation of the BSSE takes much less time than the calculation of the conformer itself. The resulting ΔE^{BSSE} values for the conformers *tGg'* and *tTt* obtained with the two methods are compared in Table VIII and Figure 7. A determination of the ΔE^{BSSE} for the 6-311+ +

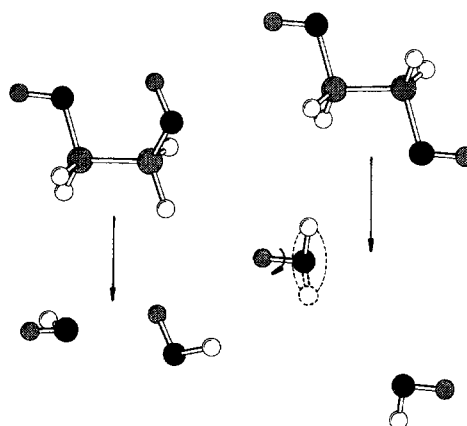


FIGURE 6. For the estimation of the BSSE of a conformer by the ecp-method. The position of the O-H-groups of a conformer are extracted and hydrogens are added. The BSSE is calculated for the resulting water dimer using the cp-method developed by Boys and Bernardi [4]. This is shown for the examples of the conformers *tGg'* (left) and *tTt* (right).

G(3*df*, 3*pd*) basis set with the acp method was not possible within a reasonable amount of computer time.

Both methods yield ΔE^{BSSE} values of the expected magnitude; the ΔE^{BSSE} determined with the ecp method is slightly larger than the one from the acp method. This may be caused by the difficulty of adding the ghost atoms properly to the conformers: The addition of ghost atoms to a conformer to mimic the nonbonded overlaps of the other conformer creates new nonbonded overlaps (dotted lines in Fig. 5), which affect the calculated BSSE. The ecp method also contains an uncertainty arising from the change of the electron distribution due to the different electronegativities of hydrogen and carbon. We performed calculations where only H—O groups were used for the estimation of the BSSE and obtained unreasonably high results due to the increased polarizability of H—O groups

TABLE VIII.
Intramolecular BSSE (kcal / mol) between Conformers *tGg'* and *tTt*, Calculated with Equivalence- and Additive Counterpoise.

	additive cp		equivalence-cp	
	HF	MP2	HF	MP2
6-31G**	0.59	1.00	0.61	1.14
D95**	0.16	0.47	0.15	0.6
TZP	0.06	0.26	0.17	0.61
TZ2P	0.05	0.16	0.09	0.29
6-311+G(2PD,2DF)	0.07	0.21	0.10	0.25

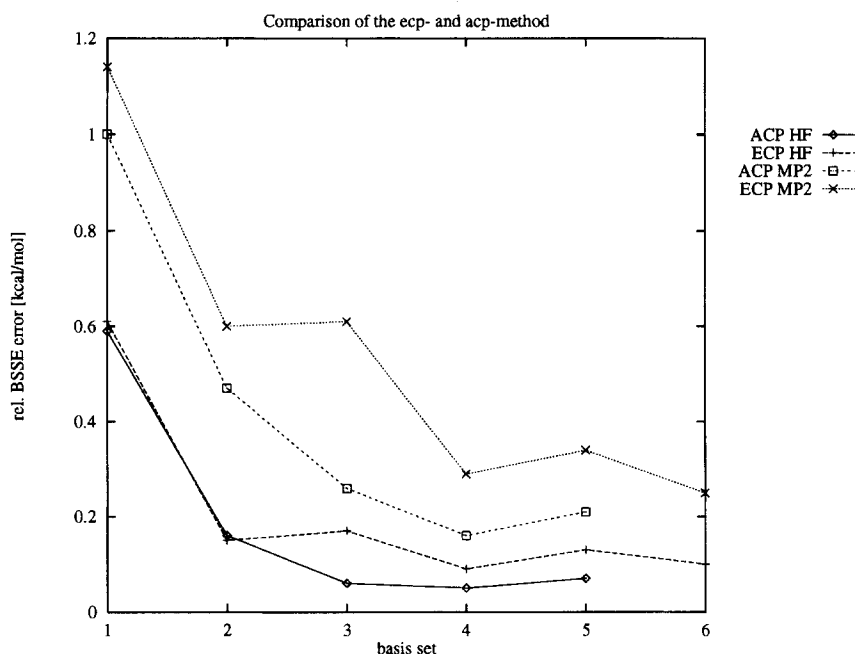


FIGURE 7. Comparison of the intra-BSSE calculated with ecp and acp. The relative BSSE is plotted against the basis set number (see Table III).

compared to a water dimer. The positioning of the added hydrogens also influences the result. We developed an automatic positioning algorithm using a molecular mechanics force field and minimizing the nonbonded interaction of the added hydrogens. During this procedure, the H—O groups extracted from glycol are kept fixed.

The increased number of basis functions (approximately 30%) is a practical disadvantage of the acp method compared with the need to calculate only pairs of conformers. The ecp method allows the calculation of the BSSE for every single conformer. Due to the stated problems, the acp

method was only used to calculate the BSSE for the *tGg'* and *tTt* conformers, while the BSSEs were calculated with the ecp method for all conformers and basis sets.

The ecp results are presented in Tables IX and X. The resulting relative energies for the conformers are shown in Figures 8 and 9. For all conformers, the corrected and uncorrected relative energies converge with increasing number of basis sets (see Fig. 10). As known from investigations on H₂O dimers, the BSSEs of the basis sets of the Dunning/Huzinaga series are smaller than those of the Pople series. The BSSEs of the MP2 energies are

TABLE IXa.
BSSE (kcal / mol) of the Glycol Conformers with Various Basis Sets, Calculated with the ecp Method on HF / 6-31G** Geometries.

	6-31G**		6-311+G(2D,2P)		6-311++G(3DF,3PD)	
	HF	MP2	HF	MP2	HF	MP2
tGg'	0.80	1.37	0.17	0.47	0.11	0.29
gGg'	0.79	1.33	0.15	0.44	0.11	0.27
g'Gg'	0.86	1.41	0.13	0.40	0.11	0.26
tTt	0.19	0.23	0.04	0.13	0.01	0.04
tTg	0.16	0.20	0.04	0.14	0.02	0.05
gTg'	0.13	0.17	0.04	0.13	0.02	0.05
gTg	0.13	0.17	0.04	0.12	0.03	0.06
gGg	0.75	1.18	0.11	0.34	0.10	0.23
tGt	0.63	0.99	0.10	0.34	0.04	0.13
tGg	0.63	1.00	0.11	0.33	0.06	0.15

TABLE IXb.
BSSE (kcal / mol) of the Glycol Conformers with Various Basis Sets, Calculated with the ecp Method on HF / 6-31G** Geometries.

	D95**		TZP		TZ2P	
	HF	MP2	HF	MP2	HF	MP2
tGg'	0.28	0.82	0.20	0.74	0.15	0.42
gGg'	0.28	0.78	0.20	0.71	0.15	0.44
g'Gg'	0.35	0.86	0.14	0.64	0.13	0.44
tTt	0.13	0.22	0.03	0.13	0.06	0.13
tTg	0.13	0.21	0.03	0.13	0.06	0.14
gTg'	0.11	0.18	0.03	0.12	0.06	0.13
gTg	0.11	0.18	0.03	0.12	0.06	0.14
gGg	0.30	0.70	0.06	0.38	0.12	0.35
tGt	0.18	0.53	0.08	0.45	0.08	0.25
tGg	0.22	0.58	0.08	0.41	0.09	0.28

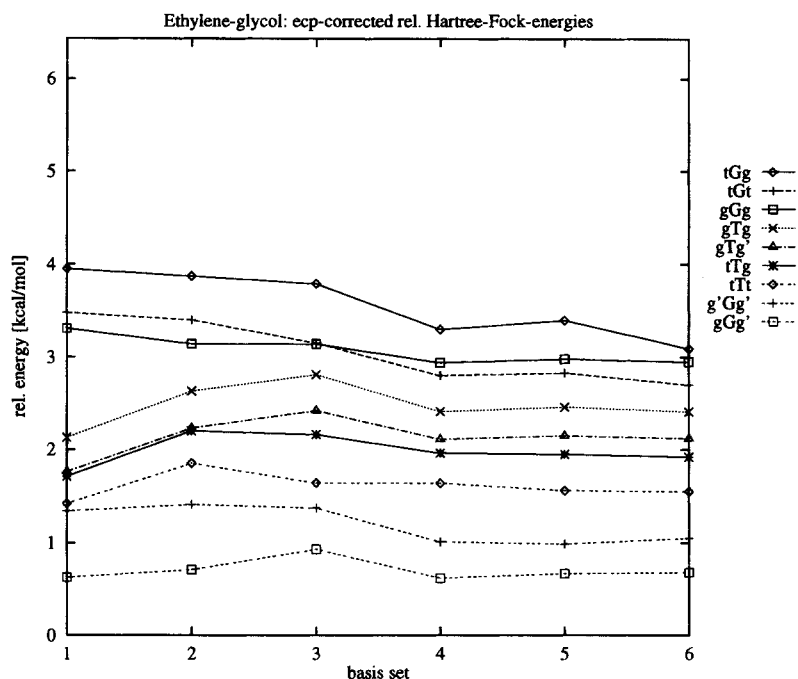


FIGURE 8. Plot of the relative ecp-corrected HF energies of the glycol conformers against the basis set number (see Table III).

larger than those of the Hartree-Fock energies, and the differences between the HF and MP2 BSSEs are larger for the basis sets of the Dunning/Huzinaga series than for the Pople series. This might occur by an overestimation of the BSSE by the cp method

used here. On the level of 6-311 + + G(3df,3pd), the BSSE is sufficiently small to be considered negligible as a source of error.

On the other hand, the BSSEs of the various basis sets cannot explain the changes in the order

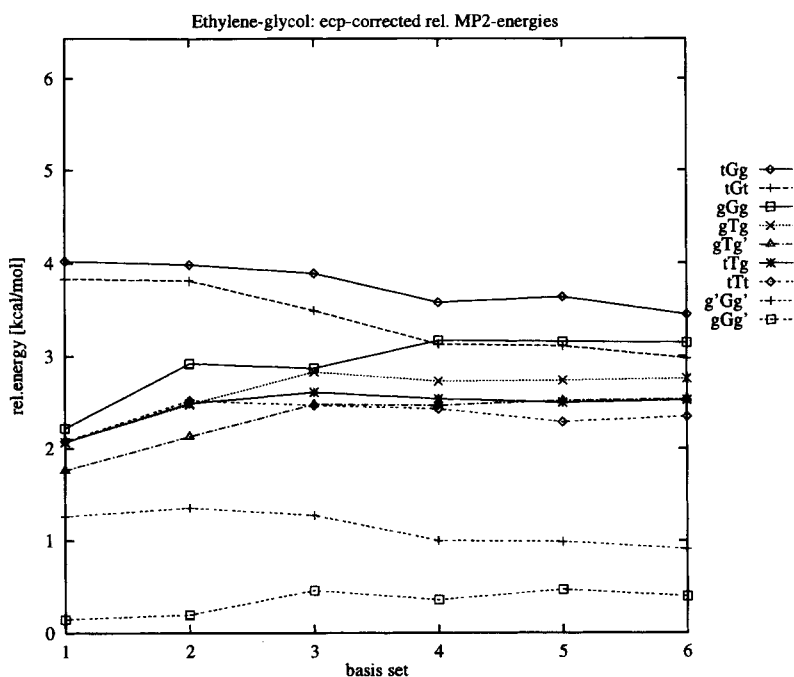


FIGURE 9. Plot of the relative ecp-corrected MP2 energies of the glycol conformers against the basis set number (see Table III).

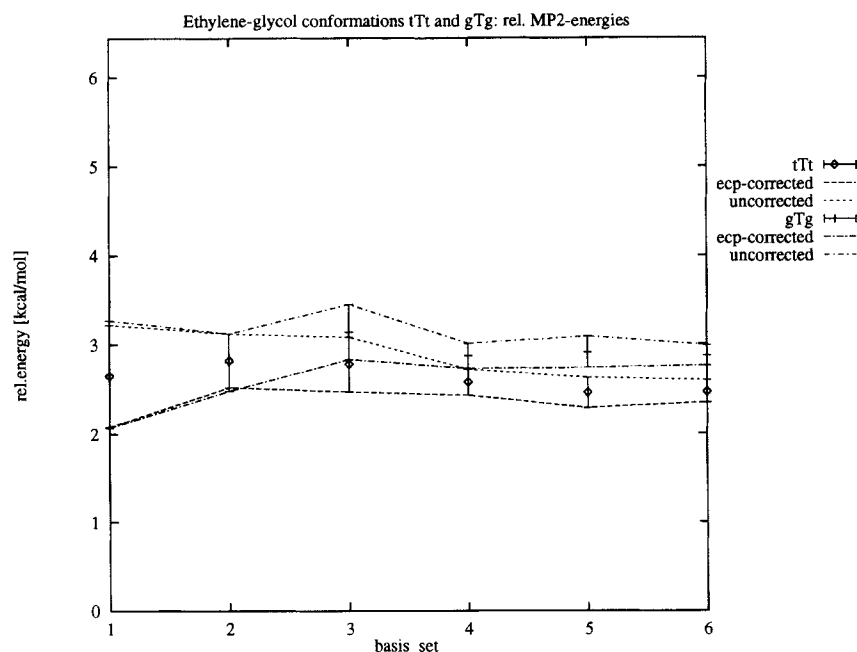


FIGURE 10. Plot of the uncorrected and ecp-corrected relative MP2 energies of the glycol-conformers tTt and gTg. For each conformer the upper line represents the uncorrected, the lower line the ecp-corrected relative energies. The basis set are depicted with their number defined in Table III.

of relative energies. The BSSEs of the four *T* conformers are nearly of the same magnitude, varying by not more than 0.06 kcal/mol. The TZ2P and 6-311 + G(2*d*, 2*p*) basis sets show a nearly identical BSSE for the four *T* conformers, but the energetical order of these conformers is changed going from TZ2P to 6-311 + G(2*d*, 2*p*).

Semiempirical Calculations

Semiempirical methods are very useful for fast and easy-to-use investigations but have the disadvantage that they are not generally applicable. For the representation of intermolecular H bonds, semiempirical methods generally fail.^{2, 27, 28} In the following section, we present results of our investigations applying semiempirical methods on 1,2-ethanediol. For this approach we used the semiempirical Hamiltonians AM1,²⁹ PM3,³⁰ and MNDO,³¹ all implemented in MOPAC 5.0.³² A full geometry optimization was performed for all 10 conformers, using the standard MOPAC minimizer and the standard convergence criteria.

DISCUSSION OF THE RESULTS

In this discussion of the results, we shall concentrate only on the relative energies of the conformers, shown in Table X, in comparison with the *ab initio* results determined on a MP2/6-311 + G(2*d*, 2*p*)/6-31G** basis. We note that the energy scales used in Table X for the three methods have different origins. This origin is defined as the lowest energy found by the particular method.

The results from the three semiempirical methods differ significantly. Each of the semiempirical methods finds a different conformer as the lowest

TABLE X.
Relative Energies (kcal / mol) of the 1,2-Ethanediol Conformers, Calculated with MNDO, AM1, and PM3 in Comparison to the MP2 / 6-311G(2*d*, 2*p*) // 6-31G Results.**

	ab-initio	MOPAC 5.0		
	MP2/6-311G(2 <i>d</i> , 2 <i>p</i>) //6-31G**	AM1	PM3	MNDO
tGg'	0.00	0.97	1.39	0.00
gGg'	0.50	0.10	0.00	1.14
g'Gg'	1.60	0.00	0.60	-> tGg'
tTt	2.63	3.95	3.94	1.26
tTg	2.83	2.53	2.45	1.53
gTg'	2.86	1.18	0.71	1.88
gTg	3.09	1.36	0.96	2.24
gGg	3.29	-> g'Gg'	0.57	1.41
tGt	3.24	-> tGg'	-> tGg'	1.17
tGg	3.78	-> tTg	3.15	1.71

in energy. AM1 favors $g'Gg'$ with its multiple H bonds. MNDO obtains tGg' as the lowest energy conformation, which is in agreement with the *ab initio* results but it is neglecting the multiple H-bonded conformer $g'Gg'$ as being stable. PM3 also determines a single H-bonded conformation as the one lowest in energy but favors the conformer gGg' with its more linear arrangement of the O—H groups over tGg' . These results confirm the work of Coitiño,²⁷ in which the same trend of the semiempirical Hamiltonians—namely, to favor multiple H bonds (AM1) and linear H bonds (PM3)—were also found. The good agreement of MNDO with *ab initio* results was also shown for the intermolecular H bonds of water dimers.

The energetical order of the four *T* conformations tTt , tTg , gTg' , and gTg is predicted in the same way by AM1 and PM3, in contrast to MNDO and *ab initio* results. The results of AM1 and PM3 differ only in the "energetical gap" between the conformations gTg' , gTg , and tTg , tTt .

All three non-H-bonded *G* conformations gGg , tGt , and tGg are found only in MNDO. Only two of those conformations are obtained with PM3 and none with AM1. PM3 reproduces the nonbonded repulsion in the conformation gGg poorly, proposing this conformation as the second stable conformation of 1,2-ethanediol and even more stable than the other two H-bonded conformations. MNDO underestimates the nonbonded interaction, leading to a lowering of the three non-H-bonded *G* conformers toward the *T* conformers. We conclude that for this case of intramolecular H bonds, MNDO seems to be the most reliable semiempirical method. All conformers of glycol are found, and the energetically most stable conformer is found in agreement with the *ab initio* results.

Conclusion

We have derived the geometries of all conformers of glycol at the HF/6-31G** level of theory. They represent all local minima of the hypersurface. It was shown that these geometries are converged within a reasonable accuracy. The geometry differences of HF/6-31G** to MP2/6-31G** are within 3° and 0.1 Å, and the energy differences are within 0.3 kcal/mol. With the derived geometries, extensive calculations with different basis sets were performed. These calculations showed that even with a "large" 6-311++G(3df,3pd) basis set, relative energy differences cannot be obtained within 0.25 kcal/mol for HF and MP2 energies because there are still drifts in the relative energies. It was shown that this can be partially attributed to an intramolecular BSSE. This BSSE does not cancel out if conformers with a different number of H bonds are compared, while the relative energies between conformers with the same number of H bonds are more reliable. We presume that this source of error becomes even more dominant in bigger molecules. Therefore, reliable hypersurfaces of large molecules with a number of possible intramolecular interactions have to be calculated with care. The BSSE will always prefer the more compact arrangement. Therefore, the strategies developed for small molecules cannot be transferred to larger molecules.

We propose two methods to evaluate and correct the intramolecular BSSE. Both methods (acp and ecp) are related to the cp method used for the intermolecular BSSE. Because of the more difficult constellation—that the molecule itself cannot be separated into two monomers—both methods can

TABLE XI.
Bond Length (in Å) of the Glycol Conformers Derived by HF / 6-31G Calculations.**

	tGg'	gGg'	$g'Gg'$	tTt	tTg	gTg'	gTg	gGg	tGt	tGg
C1-C2	1.5135	1.5167	1.5163	1.5129	1.5177	1.52177	1.5218	1.5201	1.5102	1.5153
C1-O1	1.3959	1.3954	1.4042	1.4017	1.4012	1.4007	1.3999	1.3968	1.3997	1.3967
C2-O2	1.4064	1.4078	1.4040	1.4017	1.4005	1.4007	0.9429	1.3968	1.3997	1.3971
O1-H1	0.9446	0.9449	0.9424	0.9420	0.9427	0.9429	0.9429	0.9434	0.9419	0.9430
O2-H2	0.9422	0.9434	0.9424	0.9420	0.9421	0.9429	1.0912	0.9434	0.9419	0.9423
C1-H11	1.0889	1.0925	1.0876	1.0877	1.0874	1.0863	1.0821	1.0862	1.0877	1.0825
C1-H12	1.0839	1.0844	1.0844	1.0877	1.0821	1.0863	1.0822	1.0903	1.0902	1.0908
C2-H21	1.0890	1.0883	1.0843	1.0877	1.0912	1.0863	1.0912	1.0903	1.0902	1.0905
C2-H22	1.0878	1.0826	1.0875	1.0877	1.0878	1.0863	1.0822	1.0862	1.0877	1.0924

TABLE XIII.
Torsional Angles (in degrees) of the Glycol Conformers Derived by HF / 6-31G Calculations.**

	tGg'	gGg'	g'Gg'	tTt	tTg	gTg'	gTg	gGg	tGt	tGg
O1-C1-C2-O2	60.668	57.815	57.347	180.000	180.020	-179.970	177.698	50.008	72.411	63.872
H1-O1-C1-C2	-169.957	79.243	-81.797	180.000	-175.895	73.795	70.778	45.455	-165.045	-177.916
H2-O2-C2-C1	-53.829	-45.506	-81.100	180.000	75.475	-73.795	70.787	45.971	-165.025	59.186
H11-C1-O1-H1	69.900	-47.420	157.909	61.160	64.106	-166.317	-52.569	-77.615	75.255	62.389
H12-C1-O1-H1	-50.825	-165.029	40.369	-61.160	-56.159	-49.271	-169.572	166.176	-45.210	-57.041
H21-C2-O2-H2	67.975	76.601	41.067	61.173	-47.327	166.317	-52.560	166.674	-45.190	179.193
H22-C2-O2-H2	-174.114	-166.202	158.591	-61.173	-165.007	49.271	-169.560	-77.122	75.275	-63.554

TABLE XII.
Valence Angles (in degrees) of the Glycol Conformers Derived by HF / 6-31G Calculations.**

	tGg'	gGg'	g'Gg'	tTt	tTg	gTg'	gTg	gGg	tGt	tGg
O1-C1-C2	111.3987	111.1988	111.1193	107.2715	111.3678	111.6053	111.7116	113.3179	108.9489	113.6980
O2-C2-C1	106.8837	110.6393	111.0749	107.2715	107.4699	111.6053	111.7118	113.3215	108.9494	109.2061
H1-O1-C1	107.8578	108.0751	108.8700	109.9773	109.8914	109.8624	110.0749	110.1392	110.0050	110.0150
H2-O2-C2	110.5125	109.8643	108.8917	109.9773	110.2023	109.8624	110.0748	110.1441	110.0056	110.0295
H11-C1-O1	111.1231	110.8843	110.6707	111.6219	111.8106	106.5420	111.2584	106.0026	111.4555	106.3985
H12-C1-O1	107.3267	107.5377	107.2343	111.6219	107.1450	106.5420	107.0675	111.6049	110.8260	111.1767
H21-C2-O2	111.1454	111.3142	107.2289	111.6219	111.1550	111.8580	111.2584	111.5928	110.8255	111.3080
H22-C2-O2	110.7860	106.2295	110.6589	111.6219	111.7652	111.8580	107.0645	106.0205	111.4556	111.0631

only partially correct the BSSE. While the numerical effort increases with the acp method, the ecp method seems to be a very cheap strategy to correct for the intramolecular BSSE. Here a reference calculation is performed with an equivalent arrangement of two monomers, containing less atoms. Pople and coauthors³³ recommend a minimum size of the basis set for performing reliable MP2 calculations, but here it was shown that not only the sheer size but the balance of the basis sets is important, too. We found that the results of the various basis sets converge to the final results on the level of MP2/6-311 + G(2d, 2p) // 6-31G**. So we recommend for the calculation of intramolecular H bonds that the basis set should be at least as large as 6-311 + G(2d, 2p).

Appendix A: HF / 6-31G**-derived Geometries for Glycol

Acknowledgments

This work is part of the Dr. Ing. thesis of Stephan Reiling, Technische Hochschule Darmstadt (D17). A great amount of computer time at the HLRZ Höchstleistungsrechenzentrum Jülich and at the S600 of the RWTH Rhein-Westfälische Technische

Hochschule Aachen is acknowledged. This work was supported by the Fonds der Chemischen Industrie and by AKZO Research Obermburg.

References

1. K. Szalewicz, S. J. Cole, W. Kolos, and R. Bartlett, *J. Chem. Phys.*, **89**, 3662 (1988).
2. P. Hobza and R. Zaradnik, *Chem. Rev.*, **88**, 871 (1988).
3. This naming of the basis sets is widely used. For references, see 4-21G: J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **102**, 939 (1980). 6-31G: W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972); P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973); S. Gordon, S. Chem. Phys. Lett., **76**, 163 (1980). 6-311G: R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.*, **72**, 650 (1980). D95: T. H. Dunning and P. J. Hay, In H. F. Schaefer III, *Modern Theoretical Chemistry*, vol 2, Plenum, New York, 1976. TZP: T. H. Dunning and P. J. Hay, In H. F. Schaefer III, *Modern Theoretical Chemistry*, Vol. 3, Plenum, New York, 1977, +: T. Clark, J. Chandrasekhar, G. W. Spitznagel, and P. v. R. Schleyer, *J. Comp. Chem.*, **4**, 294 (1983). *, p, d: M. J. Frisch, J. A. Pople, and J. S. Binkley, *J. Chem. Phys.*, **80**, 3265 (1984).
4. S. F. Boys and F. Bernardi, *Mol. Phys.*, **19**, 553 (1970).
5. For a review, see M. Tichy, *Adv. Organic Chem.*, **5**, 117 (1965).
6. P. I. Nagy, W. J. Dunn III, G. Alagona, and C. Ghio, *J. Am. Chem. Soc.*, **113**, 6179 (1991).
7. P. I. Nagy, W. J. Dunn III, G. Alagona, and C. Ghio, *J. Am. Chem. Soc.*, **114**, 4752 (1992).
8. S. Ikuta and O. Nomura, *Chem. Phys. Lett.*, **154**(1), 71 (1989).

9. B. J. C. Cabral, L. M. P. C. Albuquerque, and F. M. S. S. Fernandez, *Theor. Chim. Acta*, **78**, 271 (1991).
10. C. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **95**(3), 693 (1973).
11. C. van Alsenoy, L. van den Emden, and L. Schäfer, *J. Mol. Struct. (Theochem)*, **108**, 121 (1984).
12. M. A. Murcko and R. A. DiPaola, *J. Am. Chem. Soc.*, **114**, 10010 (1992).
13. G. Alagona and C. Ghio, *J. Mol. Struct. (Theochem)*, **254**, 287 (1992).
14. M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, Gaussian 90, Revision F, Gaussian, Inc., Pittsburgh, PA, 1990.
15. M. J. Frisch, J. E. Del Bene, J. S. Binkley, and H. F. Schaefer III, *J. Chem. Phys.*, **84**, 2279 (1986).
16. R. A. Friesner, *Ann. Rev. Phys. Chem.*, **42**, 341 (1991).
17. J. Dill, L. C. Allen, W. C. Topp, and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 7220 (1975).
18. S. K. Loushin, S.-Y. Liu, and C. E. Dykstra, *J. Chem. Phys.*, **84**, 2720 (1986).
19. D. W. Schwenke and D. G. Truhlar, *J. Chem. Phys.*, **78**, 4052 (1985).
20. (a) M. Gutowski, F. B. van Duijneveldt, G. Chalasinski, and L. Piela, *Chem. Phys. Lett.*, **129**, 325 (1986); (b) J. R. Collins and G. A. Gallup, *Chem. Phys. Lett.*, **129**, 329 (1986); (c) R. Eggenberger, S. Gerber, H. Huber, and D. Searles, *J. Phys. Chem.*, **96**, 6104 (1992); (d) F.-M. Tao and Y.-K. Pan, *J. Phys. Chem.*, **96**, 6105 (1992).
21. Z. Latajka, S. Scheiner, and G. Chalasinski, *Chem. Phys. Lett.*, **196**, 384 (1992).
22. Z. Latajka and S. Scheiner, *Chem. Phys. Lett.*, **140**, 338 (1987).
23. G. Alagona, C. Ghio, and J. Tomasi, *J. Phys. Chem.*, **93**, 5401 (1989).
24. G. Alagona, C. Ghio, R. Cammi, and J. Tomasi, *Int. J. Quant. Chem.*, **32**, 207 (1987).
25. J. A. Sordo, T. L. Sordo, G. M. Fernandez, R. Gomperts, S. Chin, and E. Clementi, *J. Chem. Phys.*, **90**, 6361 (1989).
26. F. J. Olivares del Valle, S. Tolosa, J. J. Esperilla, E. A. Ojalvo, and A. Requena, *J. Chem. Phys.*, **84**, 5077 (1986).
27. E. L. Coitiño, O. N. Ventura, and R. M. Sosa, *J. Mol. Struct. (Theochem)*, **254**, 315 (1992).
28. W. C. Herndon and T. P. Radhakrishnan, *Chem. Phys. Lett.*, **148**, 492 (1988).
29. M. J. S. Dewar, E. G. Zebisch, E. F. Healey, and J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).
30. J. J. P. Stewart, *J. Comp. Chem.*, **10**, 209 (1989).
31. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899 (1977).
32. J. J. P. Stewart, QCPE 455, Department of Chemistry, Indiana University, Bloomington, IN.
33. W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley & Sons, New York, 1986.